Europium doped thiosilicate phosphors of the alkaline earth metals Mg, Ca, Sr and Ba: structure and luminescence

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Abstract

Divalent europium is notorious for the tunability of its emission, depending on the host material in which it is used as a dopant. In europium-doped alkaline earth thiosilicates, two distinct emission bands can be observed for the alkaline earth metals Mg, Ca and Sr while only a single band is found for barium thiosilicate. In this work, we first complete the data with europium-doped magnesiumthiosilicate. Then, the solid solution of calcium and magnesium thiosilicate is presented. To conclude, the presence of multiple emission peaks in some compounds is explained on a structural basis, by analysing the possibilities for preferential orientation of the europium d-orbitals.

Keywords: Eu2+, thiosilicates, phosphor, Mg2SiS4, Ca2SiS4, Sr2SiS4, Ba2SiS4

1. Introduction

The luminescence of Eu^{2+} in alkaline earth thiosilicates with composition M_2SiS_4 was first reported by Avella [1] (cathodoluminescence; M = Mg,

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Ca, Sr and Ba) and Olivier-Fourcade [2] (cathodo- and photoluminescence; M = Sr, Ba). They reported one single emission peak for each alkaline earth. Avella attributed the additional peaks he observed in Mg_2SiS_4:Eu^{2+} and Ca_2SiS_4:Eu^{2+} to (trace amounts of) the binary sulfides MgS and CaS. Smet rebuked this claim for M = Ca, and showed that both Eu^{2+}-emission peaks are due to the Ca_2SiS_4-host [3]. The short-wavelength emission (565 nm) dominates at low Eu^{2+}-concentrations (<1%), while the long-wavelength peak (660 nm) does at larger concentrations. For Ba_2SiS_4:Eu^{2+}, the single emission band (500 nm) was confirmed [4]. Two distinct emission bands can be observed for Sr_2SiS_4:Eu^{2+}[5], a long wavelength peak (550 nm) and a short wavelength peak (490 nm). At room temperature, the latter is visible only for certain excitation wavelengths and for low dopant concentrations. At low temperature however, it is clearly resolved.

The scope of this work is two-fold: First, new results on the structure and photoluminescence of thiosilicate phosphors are presented. In particular, we report the photoluminescent and structural characteristics of Mg_2SiS_4:Eu^{2+} and of the solid solution $Ca_{2x}Mg_{2(1-x)}SiS_4$:Eu^{2+} with $0 \leq x \leq 1$. Then, based on both the previously published data and on the new results, a structural explanation for both the double emission bands in the thiosilicates of Mg, Ca, Sr and the single band in Ba_2SiS_4, is proposed. We can use the concept of preferential orientation of the europium 5d-orbitals to explain why there are two bands for the former, but only one for the latter.

An additional long wavelength band, next to the normal Eu^{2+} emission band, that cannot be caused by the coordination of the Eu^{2+}-sites with the anions, occurs in several other compounds [6, 7, 8, 9]. Poort et al. relate

this to a preferential orientation of one or more 5d-orbitals of Eu^{2+}, caused by the alkaline earth cations that surround the Eu^{2+}-ion. The stronger the preferential orientation, the lower the energy of the orbital becomes, and thus the longer the wavelength of the emission. They state that this preferential orientation occurs within (different types of) rows or chains. An important condition is that the interatomic distance in the row should be smaller than the distance to the next row of alkaline earth metals.

2. Experimental

The preparation of M_2SiS_4 (with M = Mg, Ca, Sr, Ba) from MS, Si and H_2S was described elsewhere [3, 4, 5]. The MgS used was 99.5 % grade (GFS Chemicals). A 5 % excess of Si was added as powder to the initial mixture, to compensate for silicon losses during sintering. Sintering temperature was 825 °C. Eu^{2+}-concentration in M_2SiS_4 was 2% in all samples. Mg_2SiS_4-samples with Eu^{2+}-concentration of 0.2%, 0.5% and 1% were also prepared.

A Bruker D5000 diffractometer in $\theta-2\theta$ geometry, was used to record XRD patterns from Cu Kα radiation.

Lattice constants and atomic positions in the unit cell were obtained using the Fullprof software package [15]. The initial parameters used for the refinement stem from various sources, an overview is given in Table 1. When data are not available, analogous structures are used as a starting point. (E.g. atomic positions of Mg_2SiS_4 were based on these of Mg_2GeS_4.)

Photoluminescence emission and excitation spectra were recorded using a FS920 fluorescence spectrometer (Edinburgh Instruments). Variation of the measurement temperature (70 K−450 K) is obtained by an Optistat CF

M^{2+}	Lattice parameters	Atomic positions	Space group
Mg	Mg_2SiS_4 [10]	Mg_2GeS_4 [11]	62 (Pnma)
Ca	Ca_2SiS_4 [3]	Ca_2GeS_4 [12]	62 (Pnma)
Sr	Sr_2SiS_4 [5]	Eu_2SiS_4 [13]	11 ($P2_1/m$)
Ba	Ba_2SiS_4 [14]		62 (Pnma)

Table 1: Overview of data used for structural analysis.

helium cryostat (Oxford Instruments) placed inside the spectrometer.

3. Results and discussion

3.1. $Mg_2SiS_4:Eu^{2+}$

As MgS is very hygroscopic (exposing it to the ambient air for one day, completely decomposes the compound), the preparation of Mg_2SiS_4 (as well as the mixtures with MgS as starting material) proved to be more cumbersome than that of the thiosilicates of Ca, Sr and Ba. All synthesized powders contain small amounts of impurities of e.g. MgS and MgO, as indicated in the XRD-data shown in Figure 1. The XRD patterns of Mg_2SiS_4 fit well to an orthorhombic structure (space group Pnma, n°62) with lattice parameters a = 12.67 Å; b = 7.41 Å; c = 5.91 Å. This result is in agreement with literature [10]. The main peaks of a simulated XRD pattern (dots) with these parameters are shown for comparison in Figure 1.

When compared with a typical XRD spectrum of the other thiosilicates (not shown), the background signal is larger in samples where Mg is present, indicating a larger amount of amorphous material. The lower quality of the

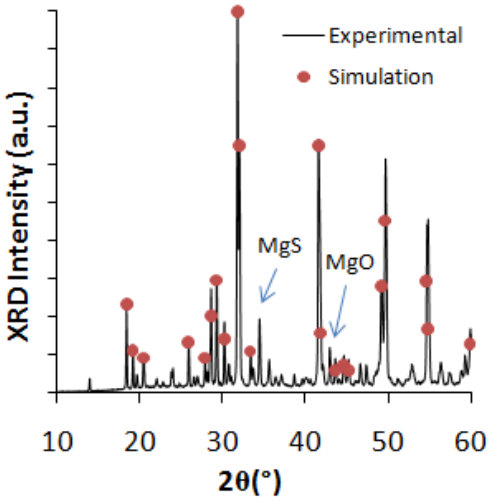

Figure 1: Measured XRD pattern (solid line) of Mg_2SiS_4:2%Eu^{2+} compared with XRD-simulation (dots). MgS and MgO impurities are also indicated.

powders that contain Mg, as compared with the other thiosilicates, can be attributed to the higher hygroscopicity of MgS.

The PL spectrum of Mg_2SiS_4:0.2% Eu^{2+} in Figure 2 consists of two emission bands peaking at 560±5 nm and 655±5 nm. Their relative intensity depends on the excitation wavelength and on the Eu^{2+}-concentration. There is a considerable overlap between the excitation spectrum of the long-wavelength band and the emission of the short-wavelength band. The intensity of the emission is low in comparison with the ones of e.g. Ca_2SiS_4:Eu^{2+} and Sr_2SiS_4:Eu^{2+} with comparable concentrations. No significant MgS:Eu^{2+}-emission (590 nm) can be identified in the spectra. Nevertheless, considering the presence of several undesired phases in small quantities, it cannot be excluded that the emission spectrum contains a small contribution originating from these phases.

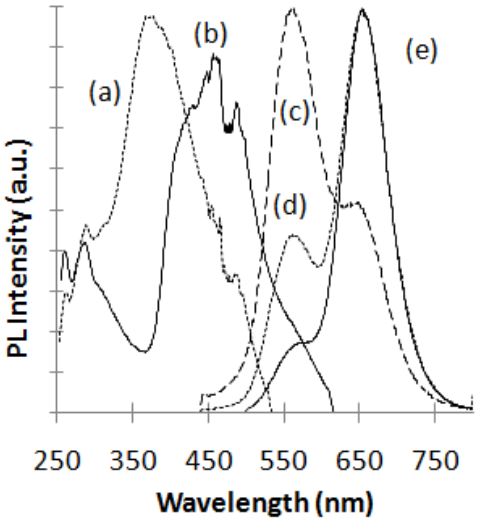

Figure 2: PL Spectrum of Mg_2SiS_4:0.2% Eu^{2+}, (a),(b) Excitation spectra monitored at 560 nm and 655 nm; (c),(d),(e) Emission spectra, excited at 365 nm, 400 nm and 450 nm

The behaviour of the emission as a function of temperature is represented in Figure 3. The short wavelength peak is rapidly quenched, dropping to half its low-temperature intensity around 265 K. The quenching behaviour of the long wavelength band is clearly different. At temperatures of >440 K, the intensity of the band has not yet dropped to half its low-temperature value. Determining a general thermal quenching temperature as the temperature at which the integrated emission intensity has dropped to half its low-temperature value, we get 400±10 K, inbetween the values for Ca_2SiS_4:Eu^{2+} (460 K) and Sr_2SiS_4:Eu^{2+} (380 K).

As the thermal quenching temperature of Mg_2SiS_4:Eu^{2+} is well above room temperature, the low intensity of the emission cannot be attributed to it being thermally quenched. The body colour of the thiosilicates doped with europium is usually very distinct, but the body colour of the doped Mg_2SiS_4-

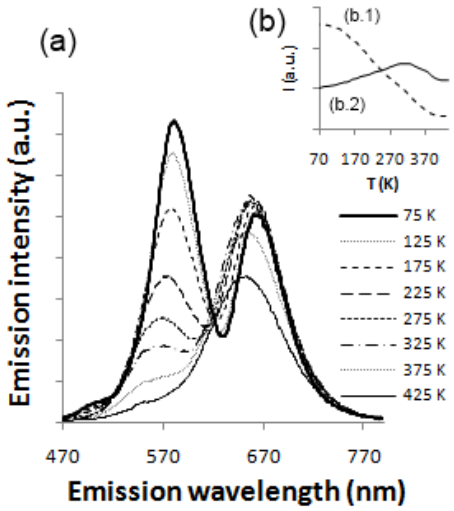

Figure 3: (a) PL Emission of Mg_2SiS_4:0.5% Eu^{2+}, excited with 400 nm light, monitored from 70 K up to 440 K (b) PL intensity as a function of temperature, (b.1) for the short-wavelength peak and (b.2) for the long-wavelength peak

samples is consistently whitish. This suggests that the Eu^{2+}-ion is poorly incorporated in this host, which does not seem implausible, considering the ion size difference between Mg^{2+} and Eu^{2+}

3.2. $(Ca,Mg)_2SiS_4:Eu^{2+}$

As both the thiosilicate of Ca and of Mg have orthorhombic P*nma* structure, it is expected that the solid solution of $(Ca,Mg)_2SiS_4$ has the same space group. The change in XRD-pattern as a function of composition is represented in both Figure 4 and Table 2. It can be seen from Table 2 that the lattice expands upon substituting Mg^{2+} by the larger Ca^{2+}. The data also indicate that up to 75 % of Mg^{2+} can replace the Ca^{2+}-ions in Mg_2SiS_4, with only a minor reduction in the dimensions of the unit cell.

The change of the photoluminescent emission as a function of compo-

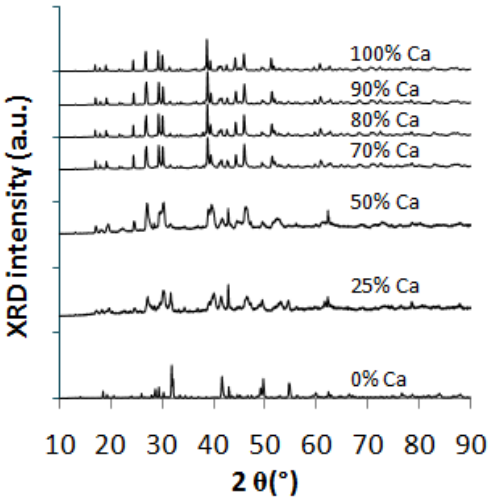

Figure 4: Measured XRD-patterns of the solid solution $(Ca_xMg_{1-x})_2SiS_4$ for x=0..1. On top is the XRD-pattern of Ca_2SiS_4, and at the bottom that of Mg_2SiS_4. In between, some intermediate compositions are shown

sition can also be found in Table 2. As an example, the PL spectrum of $(Ca_{0.5}Mg_{0.5})_2SiS_4$:2%$Eu^{2+}$ with two gaussian bands (fitting done on energy scale) is represented in Figure 5. Looking at the short wavelength peak, one notices an increase in emission wavelength, for compositions with up to 75 % of Mg^{2+}. For the fully substituted Mg_2SiS_4, the peak shifts back to shorter wavelength.

Similar to the case in MgS, the large Eu^{2+}-ion locally distorts the host lattice [16], reducing the red-shift caused by the crystal field, reducing the anticipated red-shift caused by the crystal field. **??**

3.3. M_2SiS_4:Eu^{2+} overview (M= Mg, Ca, Sr, Ba)

The thiosilicates of Mg, Ca and Sr have 2 separate emission bands. Ba_2SiS_4 has a single emission band. For all four cations, the sulfur-coordination

% Ca	a (Å)	b (Å)	c (Å)	λ_1 (nm)	λ_2 (nm)
100	13.54	8.22	6.22	565	664
90	13.52	8.18	6.20	565	663
80	13.50	8.17	6.19	566	665
70	13.49	8.15	6.18	567	659
50	13.45	8.06	6.08	581	669
25	13.41	7.81	6.05	579	643
0	12.67	7.41	5.91	560	655

Table 2: The refined lattice parameters and the emission peaks of $(Ca,Mg)_2SiS_4$:2% Eu^{2+} as a function of composition

is very similar for both alkaline earth sites. (To illustrate this, the minimum and maximum distances from the M^{2+}-ions to the nearest neighbours are given in Table 3.) In fact, in Ba_2SiS_4, the SiS_4^{4-} tetrahedra show the highest distortion, and the distances from Ba to S differ more than they do for the other thiosilicates. A difference in sulfer coordination is thus clearly not the cause of the two emission bands, as this would have the opposite effect. Also, the distance from each alkaline earth to the nearest silicon is about the same for both sites. The difference must therefore be due to the coordination of an alkaline earth site with the next one(s). Therefore, in the next paragraphs, we analyse the possibilities for preferential orientation of the divalent europium in these hosts.

The thiosilicates of Mg and Ca can be treated together, because they have a very similar structure. The lattice of both is orthorhombic, Mg (Ca) atoms are arranged in rows, at a distance of 3.71 (4.11) Å, being half the lattice

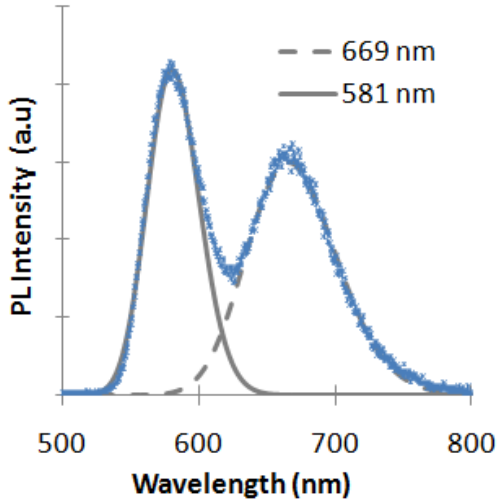

Figure 5: The emission spectrum of $CaMgSiS_4$, together with the two best fitting gaussian curves. Excitation wavelength is 400 nm.

constant along the b-axis. The distance to the next row is 5.91 (6.22) Å(the lattice constant along the c-axis), clearly larger than the distance within the row. Therefore, d-orbitals of Eu^{2+} will orient preferentially along the b-axis, thus lowering their energy and forming the long wavelength band visible in the emission spectra of Mg_2SiS_4 (Ca_2SiS_4). The Eu^{2+} d-orbitals on this crystallographic site that are not oriented preferentially, give rise to emission at shorter wavelength, as do the europium ions that occupy the second Mg (Ca) site, which is not a part of any row or chain. Therefore, no possibility for preferential orientation exists for the atoms occupying this site.

For the thiosilicate of Sr, the situation is different. The crystal structure is monoclinic, and the Sr-atoms do not line up in a perfect linear row. However, the atoms of both sites alternate at distances of 4.12 Å and 4.25 Å, the angles between the lines that connect the Sr-atoms being around 168°. This can

M^{2+}	M-S		distance	distance
	min.	max	in row(Å)	to next row (Å)
Mg	2.5	2.6	3.71	5.91
Ca	2.7	2.9	4.11	6.22
Sr	2.9	3.1	4.11/4.25	5.26
Ba	3.1	3.4	no rows	

Table 3: Key distances in the alkaline earth thiosilicate lattices.

clearly give rise to a preferential direction, along which d-orbitals of the europium-ion can orient.

Finally, in Ba_2SiS_4 no rows whatsoever can be found. Therefore, in this host there is no possibility for the Eu^{2+}-ion to orient preferentially. The emission spectrum is thus a single emission peak.

The emission spectra of all alkaline earth metals, measured at low temperature (70 K) and excited at 400 nm are shown in Figure 6. In thiosilicates, emission wavelength range from 490 nm to 660 nm (Figure 6) can be obtained by doping with Eu^{2+} and variation of the composition of the host.

4. Conclusion

The emission spectra of the solid solution $(Ca,Mg)_2SiS_4$ do not vary very much with composition. The replacement of part of the Ca^{2+}-ions in Ca_2SiS_4 by Mg^{2+}-ions proves not beneficial for practical application, since the preparation of the material is complicated by the addition of by the unstable MgS. Furthermore, several phosphor characteristics (emission intensity, thermal quenching temperature,...) deteriorate on substitution of Ca by Mg.

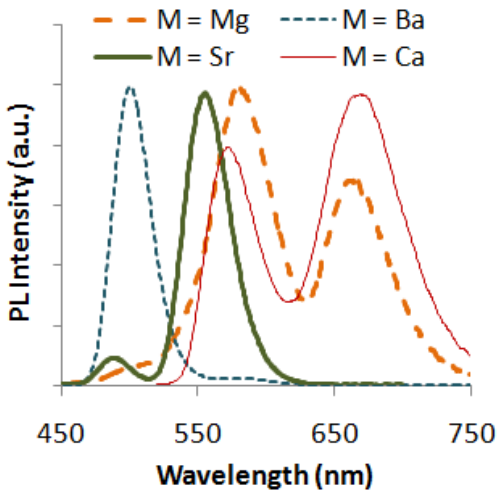

Figure 6: Normalised emission spectra of the europium-doped alkaline earth thiosilicates. The gap beween 550 nm and 660 nm can be filled with the solid solution $(Ca,Sr)_2SiS_4$.

The occurrence of two emission bands in Mg, Ca and Sr thiosilicate and the presence of only one band in Ba_2SiS_4 is explained qualitatively in terms of preferential orientation of the d-orbitals of Eu^{2+}. The difference is not due to difference in interaction with the S atoms or with the SiS_4^{4-}-tetrahedra, but it is due to a different interaction of the Eu^{2+}-ion with the nearest alkaline earth metals of the host.

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